

The activated dynamics exponent ψ for glasses

M. Barnett-Jones, M. J. Godfrey, T. Grundy and M. A. Moore

School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK

The activated dynamics exponent ψ which relates the correlation length in glasses to the alpha relaxation time is argued to equal d , the dimensionality of the system. This result is obtained via a detailed study of relaxation processes in small systems of disks confined in a square and extended to large systems by employing the mosaic picture of glasses. It is in excellent agreement with the simulational studies on hard spheres of Berthier and Witten.

PACS numbers: 64.70.P, 05.20.-y, 61.43.Fs

As the temperature T of a fragile glass is reduced, the alpha relaxation time τ_α , the fundamental glass time scale, rapidly increases. In the old theory of Adam and Gibbs [1], and the more recent random first-order transition (RFOT) theory of glasses [2], [3] and its elaboration as a mosaic picture (for a review see [4]), this increase is attributed to cooperatively rearranging regions (CRR) of size $\xi(T)$. This length scale increases as the temperature decreases and has actually been determined numerically from a study of “point-to-set” correlations [5, 6]. It is also expected to be related to the linear extent of the dynamical heterogeneities [4]. ξ and τ_α are thought to be related by the activated dynamics equation

$$\tau_\alpha \sim \tau_0 \exp[B(\xi/\sigma)^\psi], \quad (1)$$

where B is a non-universal constant, σ is a length of the order of a molecular diameter and τ_0 is a microscopic time scale. Much interest attaches to the value of the exponent ψ . In this paper we shall argue that

$$\psi = d, \quad (2)$$

where d is the dimensionality of the system. This result should hold both for hard spheres and disks, and might also extend to soft potentials. For hard spheres ($d = 3$) or hard disks ($d = 2$), the time scales and length scales are increasing functions of the packing fraction ϕ rather than the temperature [7]. In general, one expects that the correlation length grows as

$$\xi \sim \frac{\sigma}{(1 - \phi/\phi_{\max})^\nu}, \quad (3)$$

where in the approach of Fullerton and Moore [8] (see also [9]),

$$\nu = \frac{2}{d - 2\theta}; \quad (4)$$

θ is the spin glass domain wall energy exponent, and for $d = 3$ is approximately 0.2 [10–12]. ϕ_{\max} in Eq. (3) is close to (or even identical to) the random close packing fraction $\phi_{rcp} \approx 0.635$. Then, if $\psi = d$, we predict that the alpha relaxation time varies as

$$\tau_\alpha \sim \tau_0 \exp[B(1 - \phi/\phi_{\max})^{-\delta}], \quad (5)$$

where the exponent $\delta = \psi\nu = 2d/(d - 2\theta) \approx 2.3$ in three dimensions. Berthier and Witten [7] found that $\delta \approx 2.2$ in their study of hard spheres, when they used a value of $\phi_{\max} = 0.635$ for their fitting. Note that Eq. (4) applies to correlations which exist in the supercooled liquid up to alpha relaxation times. It does not apply to behavior on time scales very much longer than the alpha relaxation time, when real supercooled liquids may phase separate (if they are mixtures of species) or simply crystallize.

The basic idea of Adam and Gibbs [1] and the mosaic picture [4, 13] is that regions of size less than ξ are glassy and rarely relax. (In the simulations of Ref. [6], for cavities of a size larger than ξ the particles could escape from their initial configurations; but for cavities of size ξ or smaller, the particles were often trapped near their initial configurations when realistic, non-swap Monte-Carlo dynamics were used.) It is by a careful examination of just how the atoms within a region of linear extent $\sim \xi$ have to move in order to allow the atoms to escape from their initial configurations that we are able to argue that $\psi = d$. On the other hand, RFOT with wetting predicts that $\psi = d/2$ and $\nu = 2/d$ [2] so that $\delta = 1$, which is the Vogel–Fulcher–Tamman law [5]. If one uses the RFOT form $\nu = 2/d$, with our value of $\psi = d$, then $\delta = 2$, which is also the value obtained by the very different arguments of Schweizer [14]. The simulations in Ref. [5] were claimed to give $\psi = 1$, a value which is hard to reconcile with the value of δ of Berthier and Witten [7].

We shall illustrate the process of escape from the initial configuration for two simple systems, consisting of either two or five disks confined in a square. At high density, escape involves squeezing through a narrow neck in configuration space, which for these simple systems we can make explicit. We shall show that transition state theory provides a quantitative account of the slow relaxational processes in these small systems. The transition state theory is then generalized to large systems of hard disks or spheres, when the length scale of the dynamical heterogeneities is of order ξ , and we derive Eq. (2). (We shall assume throughout that the dynamical and static length scales are proportional when they are both large [15].) Our generalization from the explicit calculations where the number of disks, N , is small (2 or 5) to the case of

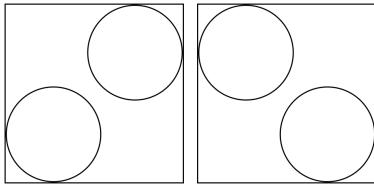


FIG. 1. Mutually inaccessible configurations of a system of two disks, illustrated for $r = 0.27 L$, which is greater than the critical value $r = 0.25 L$ below which the disks can pass each other.

large N involves assumptions about the nature and validity of the mosaic picture [4], but the good agreement for the value δ with the results of Ref. [7] suggests that the assumptions made are actually correct.

We begin with some definitions for our study of two and five disks confined in a square: L is defined as the length of one side of the square; r is the radius of the disks; and the packing fraction ϕ is defined as the fraction of the area of the square that is covered by the disks, $\phi = N\pi r^2/L^2$. A *configuration* of the disks is defined by the Nd coordinates of the disk centers (for disks $d = 2$); every configuration belongs to a *state*, which is the set of configurations that can be reached from it without violating the no-overlap constraint.

Two-disk system. The system of two disks confined to a square has been considered previously by Speedy [16]. For $r < L/4$ (or $\phi < \phi_{lg} \simeq 0.3927$) the disks can pass each other, though this becomes more difficult as $r \rightarrow L/4$. For larger values of r , the configuration space (disregarding the identity of the disks) is broken into two states in which (for $r \rightarrow L/(2+\sqrt{2})$, or $\phi \rightarrow \phi_g \simeq 0.5390$) the disk centers lie on the same diagonal of the square (see Fig. 1). These limiting configurations are the *inherent structures* introduced in Ref. [17]. Speedy [16] has considered the thermodynamics of this system and, in particular, finds weakly non-analytic contributions to the thermodynamic quantities, such as the pressure. Bowles et al. [18] have studied the dynamics of a similar system of two disks confined to a channel, and find that the mean first-passage times of the disks past each other varies as $(1 - \phi/\phi_{lg})^{-\alpha}$, where $\alpha = 2$ for inertial motion of the disks. Our event-driven molecular dynamics results (Fig. 2) confirm the value of the exponent, $\alpha = 2$, for the case of two disks in a square box.

The origin of this behavior can be obtained from transition state theory [18, 19]. In this well-studied approximation, which works best when the transition rate over a barrier is small, the transition rate R between two states varies as

$$R = 1/\tau \sim Z^\ddagger/Z, \quad (6)$$

where Z^\ddagger is the partition function evaluated at the top of the barrier; see Ref. [19] for a full description of the

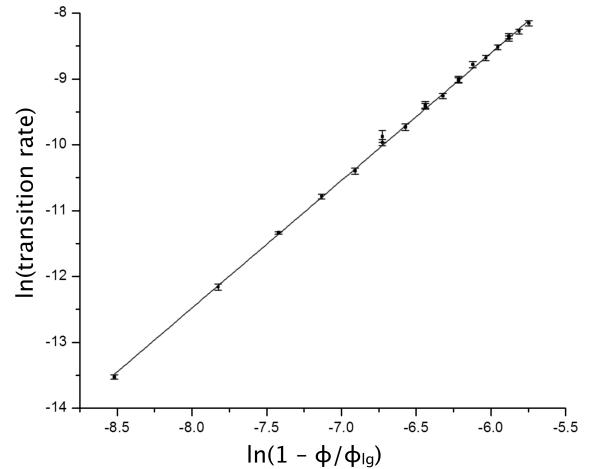


FIG. 2. Molecular dynamics transition rates ($1/\tau$) between metastable “glassy” states of the two-disk system, as the packing fraction, ϕ , approaches the critical value $\phi_{lg} \simeq 0.3927$ corresponding to $r = 0.25 L$. The gradient of the straight-line fit is 1.94, which is close to the expected value 2.

transition state formalism and the definition of Z^\ddagger . In the case of two disks passing this means that instead of the full partition function integral over (x_1, y_1) and (x_2, y_2) , there is a constraint that $y_1 = y_2 = y$, so it is effectively a three-dimensional integral. The integral over y gives a trivial factor $(L - 2r)$ and the remaining two integrals give a factor $(1 - \phi/\phi_{lg})^2$ in the limit $\phi \rightarrow \phi_{lg}$. Z itself is essentially just a constant: it has a very mild singularity, $Z_{\text{reg}} + C(1 - \phi_{lg}/\phi)^{5/2}$, when the packing fraction ϕ approaches ϕ_{lg} from above [16]. Transition state theory thus predicts a slope of 2 in Fig. 2 for the dependence of the relaxation rate on packing fraction.

Configurations of the five-disk system. The configuration space of five disks confined to a square has been analyzed previously: Bowles and Speedy [20] have discussed the thermodynamics and dynamics; Hinow [21] has studied the jammed states of this system; and Carlsson et al. [22] have given a detailed analysis of how the topology of the configuration space depends on r . We refer to Fig. 3 for configurations of the disks at two critical values of the radius.

Below the liquid–glass critical point, i.e., for $r < r_{cg} \simeq 0.1863 L$, the system is fluid (any pair of disks can exchange position), but for slightly greater values of r the configuration space is fractured into two states: a “crystalline” state in which one disk is surrounded by the four others, confined near the corners of the box; and an “amorphous” state in which all five disks lie close to the walls of the box and are unable to change their order. Above $r = r_{gg} \simeq 0.1942 L$, the state fractures further into four “frozen” amorphous states of the kind illustrated in Fig. 3 (b), in which one disk is confined near a corner of the box. Above $r = r_g \simeq 0.1964 L$, the system can exist

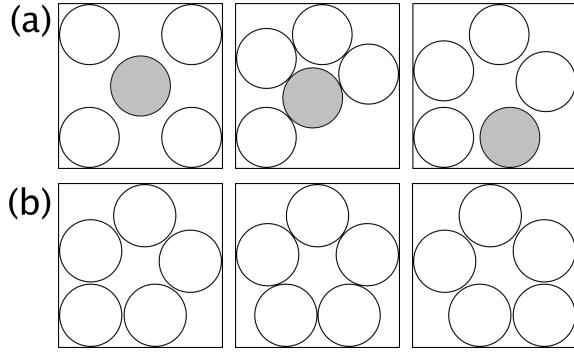


FIG. 3. (a) Representative configurations of the “crystalline” (left) and “amorphous” (right) states of a five-disk system, connected by a transition state (center), shown here with the largest radius, $r \simeq 0.1863 L$, for which the transition between crystalline and amorphous states is possible; (b) two frozen amorphous states (left and right) and the transition state (center) connecting them, shown with the maximum radius, $r \simeq 0.1942 L$, for which a transition between amorphous states is possible.

only in the crystalline state.

It may be noticed that $r_{\text{cg}} \simeq 0.1863 L$ differs significantly from the value 0.1871 stated by Carlsson et al. [22]. We have been unable to find a path between glass-like and crystal-like metastable states that passes via the configuration proposed in their paper. We find, moreover, that their proposed state with $r \simeq 0.1871 L$ is not a stationary point of the softened potential energy function E introduced in Ref. [22]: instead, it is a minimum of $|\nabla E|^2$ at which $\nabla E \neq 0$. On the other hand, we can show that our own configuration at $r \simeq 0.1863 L$ lies on a path between crystal-like and glass-like states and also that this configuration corresponds very precisely to an ordinary saddle point of E . Such a reaction path is illustrated by an animation provided in the supplement to this paper [23].

Dynamics of the five-disk system. As for the case of two disks, an event-driven molecular dynamics algorithm [24] was used to simulate the motion of the five-disk system and calculate the mean time of passage between metastable states. The initial velocities of the disks were chosen to be of fixed magnitude, but with random directions.

A very simple method was used in our work to identify when a transition had taken place. For the transition from crystal to amorphous states, the simulation is started in a typical “crystal” configuration with one disk [Fig. 3 (a), shaded] near to the center of the box. The shaded disk’s first collision with any wall is an unambiguous sign that the transition to the amorphous state has occurred. Transitions between metastable amorphous states can be identified in a similar way, using the fact that every disk remains near the perimeter of the box. From Fig. 3 (b), we can see that a transition has occurred

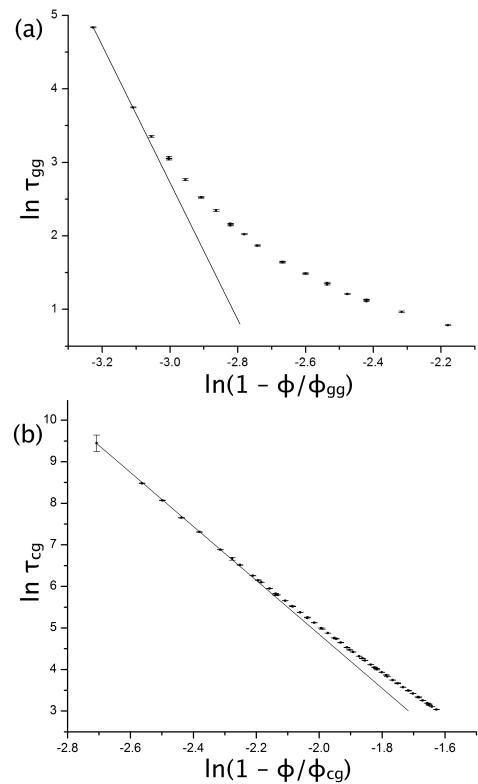


FIG. 4. Molecular dynamics transition times: (a) between two amorphous states; (b) between the crystalline and amorphous states. Both graphs have a noticeable curvature: the steepest gradients are approximately (a) -9 and (b) -6.5 .

if any disk makes a collision with a wall other than the one (or two) it was close to in the initial configuration. For each kind of transition, the time of first occurrence of the diagnostic event is recorded and the simulation restarted with random initial velocities.

Results from our simulations are plotted in Fig. 4. They show that, as expected, the mean time of passage increases rapidly as ϕ approaches a critical value $\phi_c = \phi_{\text{cg}}$ or ϕ_{gg} . Because of the slowing-down of the dynamics, our simulations were unable to reach a regime where a power-law dependence of τ on $(1 - \phi/\phi_c)$ could be demonstrated unambiguously: the steepest gradients in the graphs of Fig. 4 (a) and (b) are approximately -9 and -6.5 , respectively. The first of these results (for the transition between metastable amorphous states) is easy to understand in the transition-state theory. If the reaction coordinate is fixed at the value it takes in the transition state, the hard-disk constraints define a configuration space with nine spatial dimensions: accordingly, the constrained partition function (and hence τ_{gg}^{-1}) should be expected to vary as $(1 - \phi/\phi_{\text{gg}})^9$; we have verified this dependence by a separate Monte Carlo sampling of the partition function. A similar argument could, of course, be made for the transition between metastable

crystal and amorphous states, if ϕ was sufficiently close to ϕ_{cg} ; our results from molecular dynamics suggest that the anticipated power-law behaviour is restricted to a very narrow range of ϕ and that this asymptotic regime was not reached in our simulations.

Our conclusion from these studies is that a transition between states in a region containing N particles generally requires coordinated motion of all the N particles in order to squeeze through the neck in the phase space. The rate at which this will occur is, according to transition state theory,

$$1/\tau \sim (1/\tau_0)(1 - \phi/\phi_{\text{Neck}})^{Nd-1}/(1 - \phi/\phi_J)^{Nd}, \quad (7)$$

where ϕ_J is the packing fraction of the jammed state closest to the initial configuration of the particles and ϕ_{Neck} is the highest packing fraction below ϕ_J at which a neck first opens to allow escape from the jammed state. In studies of jammed states in large systems, Torquato and Jiao [25] found an algorithm which generated jammed states over a wide range of packing fractions. (The commonly used Lubachevsky-Stillinger algorithm [26] mainly produces jammed states with $\phi_J \approx 0.635$. When the number of particles is small, the value of ϕ_J is reduced and the distribution of the range of ϕ_J broadens [27].) We attribute the slow dynamics in the system to the squeezing through narrow necks in the configuration space which is required to escape from the vicinity of the initial conditions.

The key to the derivation of our main result, $\psi = d$, is the following picture of the allowed configuration space of N hard spheres or disks in a box. Consider spheres. As the packing fraction increases beyond $\phi \approx 0.59$, there is marked slowing down of the dynamics of the system; τ_α grows rapidly as the packing fraction increases past this density: the spheres are caged and can only escape from the cages on the alpha relaxation time scale. We are imagining that typical initial conditions place the system close to one of the jammed states but that there is a way of escaping from this state through a neck in configuration space. Suppose that the packing fraction ϕ is close to but below ϕ_{Neck} . Let

$$a = \ln \left[\frac{1 - \phi/\phi_J}{1 - \phi/\phi_{\text{Neck}}} \right] / d, \quad a > 0, \quad (8)$$

then from Eq. (7), provided N is large,

$$\tau \sim \tau_0 \exp[aN]. \quad (9)$$

Note that the form of the equation (i.e. its dependence on N) would be hardly altered if a finite fraction of the N particles were rattlers.

The next step in the argument is to apply Eq. (9) in the context of the mosaic picture of dynamic heterogeneity [28]. The scale of the tiles within the mosaic is ξ . It is pictured that the dynamics of glasses proceeds by a

series of rearrangements in each tile. Once in one tile the atoms have reached a different state; this will sometimes trigger state changes in neighboring tiles. Such avalanches of movement are commonly observed [28]. To rearrange the spheres in a region of size ξ a neck will have to be passed through in phase space and the time scale for doing this will be as given in Eq. (9) but with N replaced by the number of spheres in the region of size ξ which is $\sim (\xi/\sigma)^d$. Different regions will have different values for a , which is in accord with the fact that there is a spread of relaxation times associated with the dynamic heterogeneities [28]. The alpha relaxation time sets the time scale for these processes, so in Eq. (1) it follows that $\psi = d$. Note that the mosaic size ξ is the size of the region on which one has to make re-arrangements in order to allow an atom to escape from its surrounding cage, so that the timescale τ is naturally identified in this picture with the alpha relaxation time.

We should like to thank Chris Fullerton for many useful discussions.

-
- [1] G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
 - [2] T.R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, *Phys. Rev. A* **40**, 1045 (1989).
 - [3] V. Lubchenko and P.G. Wolynes, *Ann. Rev. Phys. Chem.* **58**, 235 (2006).
 - [4] L. Berthier and G. Biroli, *Rev. Mod. Phys.* **83**, 587 (2011).
 - [5] C. Cammarota, A. Cavagna, G. Gradenigo, T. S. Grigera and P. Verrocchio, *J. Chem. Phys.* **131**, 194901 (2009); *J. Stat. Mech. L* 12002 (2009).
 - [6] A. Cavagna, T. S. Grigera, and P. Verrocchio, *J. Chem. Phys.* **136**, 204502 (2012).
 - [7] L. Berthier and T. A. Witten, *Phys. Rev. E* **80**, 021502 (2009).
 - [8] C. Fullerton and M. A. Moore, to be published.
 - [9] M. A. Moore and J. Yeo, *Phys. Rev. Lett.* **96**, 095701 (2006).
 - [10] A.J. Bray and M. A. Moore, *J. Phys. C: Solid State Physics* **17**, L463 (1984).
 - [11] A. K. Hartmann, A. J. Bray, A. C. Carter, M. A. Moore, and A. P. Young, *Phys. Rev. B* **66**, 224401 (2002).
 - [12] S. Boettcher, *Phys. Rev. Lett.* **95**, 197205 (2005).
 - [13] G. Biroli and J-P. Bouchaud, *Europhys. Lett.* **67**, 21 (2004).
 - [14] K. S. Schweizer, *J. Chem. Phys.* **127**, 164506 (2007).
 - [15] W. Kob, S. Roldán-Vargas, and L. Berthier, *Nature Physics*, **8**, 164 (2012).
 - [16] R. J. Speedy, *Physica A* **210**, 341 (1994).
 - [17] F. H. Stillinger, E. A. DiMarzio, and R.L. Kornegay, *J. Chem. Phys.* **40**, 1564 (1964).
 - [18] R. K. Bowles, K. K. Mon, and J. K. Percus, *J. Chem. Phys.* **121**, 10668 (2004).
 - [19] G. Mazzola, S. A. Beccara, P. Facciola, and H. Orland, *J. Chem. Phys.* **134**, 164109 (2011).
 - [20] R. K. Bowles and R. J. Speedy, *Physica A* **262**, 76 (1999).
 - [21] P. Hinow, *Optim. Letters* (accepted for publication, 2012). [arxiv:math/00/1209.4053](https://arxiv.org/abs/math/00/1209.4053)

- [22] G. Carlsson, J. Gorham, M. Kahle, and J. Mason, Phys. Rev. E **85**, 011303 (2012).
- [23] http://www.theory.physics.manchester.ac.uk/~godfrey/supplement/activated_dynamics.html
- [24] B. D. Lubachevsky, J. Comp. Phys. **94**, 255 (1991).
- [25] S. Torquato and Y. Jiao, Phys. Rev. E **82**, 061302 (2010).
- [26] B. D. Lubachevsky and F. H. Stillinger, J. Stat. Phys. **60**, 561 (1990).
- [27] N. Xu, J. Blawdziewicz, and C. S. O'Hern, Phys. Rev. E **72**, 019901 (2005).
- [28] L. Berthier, Physics **4**, 42 (2011).